

# PATENT SPECIFICATION

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## (54) IMPROVEMENTS IN OR RELATING TO SILICA-BASED DEFOAMER COMPOSITIONS

(71) We, DIAMOND SHAMROCK CORPORATION, of 1100 Superior Avenue, Cleveland, Ohio 44114, United States of America, a corporation organised and existing under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to stabilized silica-based defoamer compositions and their use in aqueous systems.

Silica-based defoamers are well known as defoamers for aqueous systems. One of the problems of such defoamers, however, is the tendency for the silica particles to settle out of the carrier liquid (usually a hydrocarbon or natural oil) in which they are suspended. Only the use of extremely fine particle silica achieves some degree of stability. However, fine particle silica is of limited supply and is more expensive than other grades.

Quick-chilled amides are also well known as defoamers for aqueous systems. In addition, it is known to use mixtures of silica and quick-chilled amides, where each is present in defoaming quantities.

The following patents disclose the defoaming properties of various components of the subject compositions, but none discloses their combination for the purpose of increasing the stability of silica-based defoamers.

United States Patent No. 3,076,768 (Boylan) discloses silica-based defoamers containing hydrophobic silica, hydrocarbon oil, and a spreading agent.

United States Patent No. 3,207,698 (Liebling and Canaris) discloses silica-based defoamers containing hydrophobic silica of a particular nature and hydrocarbon oil.

United States Patent No. 3,652,453 (MacDonnell) discloses amide-based defoamers containing quick-chilled amides,

hydrocarbon oil, and oil-soluble organic polymers.

United States Patent No. 3,677,963 (Litchman and Rosengart) discloses amide-based defoamers containing quick-chilled amides, hydrocarbon oil, oil-soluble organic polymers and fats.

According to one aspect of this invention, a defoamer composition comprises a suspension of 3% to 20% by weight of hydrophobic silica in a water-immiscible carrier liquid and, as a stabilizer for the suspension, 0.1% to 2.0% by weight of a quick-chilled amide.

Optionally, oil soluble organic polymers and surface-active additives may be added.

A process of manufacture of a hydrophobic silica-based defoamer, according to this invention, comprises forming a temporarily stable suspension of hydrophobic silica in a water-immiscible carrier liquid heated to at least 100° C., cooling the suspension to room temperature or below, separately heating an amide optionally mixed with a water-immiscible carrier liquid until the amide is melted or is dissolved in the carrier liquid, maintaining the amide as a melt or solution at elevated temperature for at least 15 minutes, rapidly adding the amide to the suspension, so as to quick-chill the amide, and homogenizing the resultant hydrophobic silica/carrier liquid/quick-chilled amide mixture at a pressure of 1,000 to 5,000 p.s.i., the resulting suspension containing 3% to 20% by weight of the silica and 0.1% to 2.0% by weight of the amide.

The silica must be rendered hydrophobic, by roasting with silicone oil or by other means. The hydrophobic silica and oil contain almost the entire defoaming properties of these compositions.

The amide, which must be quick-chilled as described herein, is used solely for stabilizing the defoamer composition. That is, it has been unexpectedly discovered that the addition of a small quantity of quick-chilled amide

acts to stabilize the defoamer by keeping the silica particles in suspension for a considerably longer time than in its absence. Of course, the quick-chilled amide does possess defoaming capabilities of its own. However, the amount of quick-chilled amide used is not sufficient to increase the effectiveness of the defoamer appreciably.

The defoamer compositions of this invention may be manufactured by simply mixing the fully prepared ingredients or may be prepared partially in situ.

The compositions of this invention are useful to some degree in almost all aqueous systems in which defoaming is a problem. Such uses include: boiler water; sugar beet refining; paper manufacture; textile manufacture; adhesives; cement; and coatings. These defoamer compositions are particularly useful in defoaming the black liquor found in paper pulp processing, and for the prevention of air entrainment in water-base paints and adhesives.

The hydrophobic silica useful in this invention may be prepared from any of the well-known forms of silica such as: (1) silica aerogel, a colloidal silica which may be prepared by displacing the water from a silica hydrogel by a low-boiling, water-miscible, organic liquid, heating, e.g. in an autoclave, above the critical temperature of the liquid, and then venting the autoclave, (2) so-called fume silica, a colloidal silica obtained by burning silicon tetrachloride and collecting the resulting silica smoke, (3) a precipitated silica prepared by the destabilization of a water-soluble silica under conditions which do not permit the formation of a gel structure, but rather cause the flocculation of silica particles into coherent aggregates such as by the addition of sodium ions to a sodium silicate solution; as well as aluminum silicate, copper silicate, magnesium silicate and zinc silicate. Almost any grade and particle size of silica is useful although finer particles are preferred. Hydrophilic inorganic particles which might be expected to be silica substitutes such as calcium hydroxide, magnesium hydroxide and calcium carbonate were found not to be useful.

Any suitable method may be employed for treating the normally hydrophilic silica to render it hydrophobic. One method which has proved very satisfactory involves spraying the silica with silicone oil and heating at elevated temperature, i.e., from about 250° C. to about 350° C. for about 1/2 to about 2 hours. The amount of silicone oil utilized may vary from about 5% to about 100% by weight based on the weight of the silica. However, amounts from about 7% to about 25% will usually be satisfactory and are preferred.

The term "silicone oil" in this specification means a polysiloxane oil such as an alkyl, aryl, alicyclic or aralkyl siloxane or polysil-

oxane having a viscosity of from about 10 to about 3000 centistokes at 25° C. Preferred silicone oils include alkyl polysiloxanes having viscosities of from about 40 to about 100 centistokes at 25° C. These alkyl polysiloxanes include dimethyl polysiloxane, diethyl polysiloxane, dipropyl polysiloxane, methyl ethyl polysiloxane, dioctyl polysiloxane, dihexyl polysiloxane, methyl propyl polysiloxane, dibutyl polysiloxane and dodecyl polysiloxane.

The finely divided silica may also be rendered hydrophobic by treatment with vapors of an organo-silicon halide or mixture of organo-silicon halides. Examples of organo-silicon halides suitable for this purpose are given in United States Patents Nos. 2,306,222 and 2,412,470 and include alkyl (methyl), aryl (phenyl), alkaryl (tolyl) and aralkyl (phenyl methyl) silicon halides. The treatment may be carried out by agitating the finely divided material in a closed container in the presence of vapors of the treating material, e.g., dimethyl dichlorosilane. The amount of treating material and the length of treatment will depend upon the surface area of the inorganic material and the nature of the organo-silicon halide employed. In general, it will be satisfactory to use from about 5% to about 15% by weight of treating agent based on the weight of silica and a time of treatment from about 1/2 hour to about 2 hours.

Still another method of rendering the silica hydrophobic is by dispersing it in silicone oil, i.e., in a concentration from 2—10% and heating the dispersion to 250—300° C. for about an hour. The hydrophobic silica may then be extracted by centrifuging the mixture after dilution with hexane or a similar type of solvent and drying the resulting solid.

The hydrophobic silica utilized will desirably have an average particle size less than 10 microns and preferably less than 5 microns. Most preferred is an average particle size from 0.02 micron to 1 micron.\*

The carrier liquid can be any substance which is inert towards the other ingredients, immiscible with water, liquid at room temperature and atmospheric pressure, and which has a viscosity of from about 30 to about 400 SUS (Saybolt Universal Seconds at 38° C.)

Although any substance meeting the above criteria can be used, the preferred carrier liquids are natural oils, mineral oils and hydrocarbons.

\*Measuring the particle size in terms of Oil Absorption Value, 125 (grams of oil absorbed per 100 grams of silica) is the minimum useful value and a value of 170 or higher is preferred.

Examples of preferred carrier liquids include, but are not limited to: mustard seed oil, castor oil, rice bran oil, soya oil, corn oil, mineral seal oil, stoddard solvent, petroleum naphtha, paraffinic mineral oil, naphthenic mineral oil, toluene, xylene, benzene, hexane, heptane, octane, dodecane and kerosene. If desired, mixtures of two or more carrier liquids can be used. An especially preferred carrier liquid is paraffinic mineral oil.

It should be noted that the carrier liquid when used in quick-chilling the amide must have a minimum boiling point equal to the melting point of the amide and an average of from about 6 to about 25 carbon atoms.

Quick-chilled amides which are especially useful in carrying out the invention include those obtained by reaction of a polyamine containing at least one alkylene group having from two to six carbon atoms and a fatty acid having from six to eighteen carbon atoms. One example is the amide obtained by reaction of a polyamine and a fatty acid or mixture of fatty acids such as hexanoic, decanoic, lauric, palmitic, oleic, and stearic acids, hydroxy acids such as ricinoleic acid, or naphthenic acids such as are obtained as byproducts from the refining of petroleum. Natural mixtures of fatty acids such as tall oil acids and tallow fatty acids also can be used. Suitable amines include ethylene diamine, butylene diamine, diethylene triamine, triethylene tetramine, hexamethylene diamine, decamethylene diamine, hydroxyethyl ethylene diamine and 1:3-diamine-2-propanol.\*

One of the amides useful herein is prepared in the following manner. 95.7 parts by weight of bleached-hydrogenated tallow fatty acids is charged into a stainless steel reactor with a condenser, water trap and agitator. The entire process including charging of reactants and cooling of the reaction product is carried out under a nitrogen atmosphere. The acids charge is heated to about 165—175° C. and 10.1 parts by weight of ethylene diamine is added with agitation. After the diamine is added, the reaction mixture is heated to about 180—185° C. The mixture is reacted at about 180—185° C until the acid value is less than 5 and the alkalinity less than 0.6% by weight. The resulting reaction product of ethylene diamine and tallow fatty acid is then cooled to room temperature. If desired, the cooled mass can be ground to obtain the product in the form of a very fine powder.

The "Quick-Chilling" Process is essentially the same as that described in United States Patents Nos. 3,652,453 and 3,677,963, which descriptions are hereby incorporated by reference. The difference between the quick-chilling processes in the above patents and the process used in this invention is that in this

invention the amide is not combined with other ingredients in the melt other than the carrier liquid. The quick-chilling process consists of heating the amide to above its melting point, maintaining the amide in a molten state for at least 15 minutes, and then rapidly quick-chilling the amide by: (a) adding a colder carrier liquid or water; (b) rapidly dropping the melt into colder carrier liquid; or (c) applying the melt to a cold surface and adding the resulting coagulate to a carrier liquid. Optionally, the amide may be mixed with some of the carrier liquid before heating, in which case the mixture should be heated to a temperature where the amide is fully dissolved and then maintained at that temperature for at least 15 minutes. It is important in either case that the amide be heated long enough for any crystalline nuclei to be destroyed, so that the amide may more readily assume the desired new crystalline structure formed by the quick-chilling process. The term "colder" is defined as room temperature (22° C) or below.

Almost any oil soluble polymers are useful to some degree in this formulation and include vinyl acetate co-polymerized with ethylenically unsaturated comonomers which are copolymerizable therewith such as maleic and fumaric acid esters, ethylene, propylene and butylene; polyalkylene oxide adducts such as methyl glucoside propoxylated with four moles of propylene oxide; glycerine propoxylated with fifteen moles of ethylene oxide and forty-five moles of propylene oxide; the copolymer of lauryl methacrylate and vinyl pyrrolidone; methacrylate copolymers dissolved in solvent-refined (100 SUS at 38° C) neutral oil; and phenol modified coumarone-indene resins. These materials can be used alone or in admixture with each other.

One oil soluble polymer which is preferred is a copolymer of vinyl acetate and fumaric acid esterified with a tallow alcohol. Such an oil soluble polymer is available from Enjay Chemical Co. in the form of a mineral oil solution thereof under the trademark "Paratone 440" which consists of about 25 parts by weight of said copolymer in 75 parts by weight of a liquid hydrocarbon. This product has the following properties:

Viscosity at 98.9° C. cs	1300
Flash point, CPC, °C.	182
Color, ASTM	40
Specific Gravity at 15.6° C.	0.92

Another preferred oil soluble polymer is a copolymer of styrene and a polyester. Such an oil soluble polymer is available from The Lubrizol Corporation in the form of a paraffin oil solution thereof under the trademark "Lubrizol 3702" which consists of about 30 parts by weight of said copolymer in 70 parts by weight of liquid hydrocarbon. This product has the following properties:

\*Monoamines are not useful in this invention.

Viscosity at 98.9° C. SUS	3800
Viscosity at 98.9° C. cs	815
Specific Gravity at 15.6° C.	0.905

5 Still another preferred oil soluble polymer is a copolymer of alkyl methacrylate and N-vinyl pyrrolidone. Such an oil soluble polymer is available from Rohm and Haas Company in the form of a neutral oil solution thereof under the trademark "Acryloid 966" which consists of about 30 parts by weight of said copolymer in 70 parts by weight of liquid hydrocarbon. This product has the following properties:

Viscosity at 98.9° C. SUS	3730
Viscosity at 98.9° C. cs	800
Flash Point, CPC, ° C	192.5
Color, ASTM	3
Specific Gravity at 15.6° C	0.899

20 When an oil soluble polymer is used, the amount of hydrophobic silica may be reduced to about 4 to 7% by weight in order to lower the viscosity. The defoaming efficacy of the composition remains the same despite the reduction. The acceptable viscosity range for the compositions of this invention is 200 to 2,000 cs, with a preferred range of 400 to 600 cs.

30 Optional surface-active additives useful in this invention may function as spreading and/or emulsifying agents and may be anionic, cationic or nonionic. The particular type of surface-active additive to be utilized is determined to some extent by the type of system in which it is used. In general, the anionics appear to give the best defoaming efficiencies and are preferred. Examples of suitable anionics are fatty acids containing from about 12 to about 22 carbon atoms such as stearic and soaps of these fatty acids such as the alkali metal, alkali earth metal, aluminum, ammonium and amine soaps, e.g., triethanolamine stearate, as well as rosin soaps. The soaps may be added as such or formed in situ. Examples of other suitable anionics are alkali metal salts of alkyl-aryl sulfonic acids, sodium dialkyl sulfo-succinate, sulfated or sulfonated oils, e.g., sulfated castor oil, sulfonated tallow, and alkali metal salts of short chain petroleum sulfonic acids.

50 Examples of suitable cationics are salts of long chain primary, secondary, or tertiary amines, such as oleylamine acetate, cetylamine acetate, di-dodecylamine lactate, the acetate of monostearoyl diethylene triamine, dilauryl triethylene tetramine diacetate, 1-aminoethyl-2-heptadecenyl imidazoline acetate; and quaternary salts, such as morpholinium ethyl sulfate, cetylpyridinium bromide, hexadecyl ethyl morpholinium chloride, and diethyl di-dodecyl ammonium chloride.

60 Examples of suitable nonionics are silicone oils as defined herein, condensation products

of higher fatty alcohols with ethylene or propylene oxide, such as the reaction products of butyl alcohol with 30 propylene oxide units or of cetyl alcohol with 8 ethylene oxide units; 65 condensation products of alkylphenols with ethylene oxide, such as the reaction product of isooctylphenol with 12 ethylene oxide units; 70 condensation products of higher fatty acid amides with 5 or more ethylene oxide units; polyethylene glycol esters of long chain fatty acids, such as tetraethylene glycol monopalmitate, hexaethyleneglycol monolaurate, nonaethyleneglycol monostearate, nonaethyleneglycol dioleate, tridecaethyleneglycol monoarachidate, tricosathylene glycol monobenhenate, tricosathyleneglycol dibehenate, ethylene oxide condensation products of polyhydric alcohol partial higher fatty acid esters, and their inner anhydrides (e.g. mannitol-anhydride and sorbitol-anhydride), such as glycerol monopalmitate reacted with 10 molecules of ethylene oxide, pentaerythritol monooleate reacted with 12 molecules of ethylene oxide, sorbitan monostearate reacted with 10 to 15 molecules of ethylene oxide; 85 mannitan monopalmitate reacted with 10 to 15 molecules of ethylene oxide; long chain polyglycols in which one hydroxyl group is esterified with a higher fatty acid and the other hydroxyl group is esterified with a lower alcohol, such as methoxypolyethylene glycol 550 monostearate (550 meaning the average molecular weight of the polyglycol ether). Combinations of two or more surface-active additives may be used provided that anionics are not blended with cationics. 95

100 In a partial in situ method of preparation, the hydrophobic silica is first mixed with the carrier liquid, which has been heated in order to keep the silica particles in suspension. The suspension is then cooled to room temperature or below and the amide (optionally containing some carrier liquid) which has been melted and maintained as a melt (or solution) for at least 15 minutes, is quick-chilled by rapidly adding it to the suspension. The suspension/amide mixture is then homogenized preferably while at room temperature, at a pressure of 1,000 to 5,000 p.s.i., preferably 1,500 to 3,250 p.s.i., and particularly preferably at 3,000 p.s.i. Homogenization can also be undertaken while the mixture is at a higher temperature, in which case the pressure can be higher. Unexpectedly, it was discovered that the homogenization can be at a higher pressure for a silica/carrier liquid/amide mixture than for a carrier liquid/amide mixture. After homogenization, the oil soluble polymer and surface-active additive may optionally be added. 115 120

125 In a simple mixture method of preparation, the hydrophobic silica is first mixed with the carrier liquid which has been heated in order to keep the silica particles in suspension. The suspension is then cooled to room tempera-

ture. The amide, which has already been quick-chilled separately, is then simply mixed with the suspension and the mixture is homogenized and optional ingredients are added, in the same manner as above. Alternatively, the quick-chilled amide-carrier liquid mixture and the silica/carrier liquid mixture may be homogenized separately and then blended, in which case further homogenization is not necessary.

All of the following ingredient parameters are in terms of % by weight based upon a 100% composition.

The hydrophobic silica should be present in from 3 to 20%, and preferably 4 to 11%.

The quick-chilled amide should be present in from 0.1 to 2.0% and preferably 0.8 to 1.2%.

The oil soluble polymer may be present in up to 25% and preferably 8 to 12%.

The surface-active additive may be present in up to 3.0% and preferably 0.5 to 2.5%.

The carrier liquid is present in the amount which is the difference between all of the above ingredients and 100%.

#### EXAMPLE I.

Nine parts (36 g) of hydrophobic silica having a mean particle diameter of 22 microns were added to 75.5 parts (302 g) of paraffinic mineral oil which had been heated to 100° C. After agitation, the mixture was cooled to room temperature (about 22° C) forming a silica in oil suspension of limited stability. One half part (2.0 g) of an amide comprising the reaction product of ethylenediamine and tallow fatty acid was mixed separately with 15 parts (60 g) of mineral oil, heated to 140° C, and maintained at that temperature for 15 minutes. The amide/oil mixture at 140° C was then quick-chilled by rapidly adding it to the silica/oil suspension at 22° C, forming a mixture of hydrophobic silica, quick-chilled amide, and mineral oil. The mixture was then homogenized to achieve a uniform suspension.

#### EXAMPLE II.

A composition was prepared according to Example I with the following exceptions. Ten parts of silica was suspended in 75.5 parts of mineral oil, 1.0 part of amide was melted with 10 parts of mineral oil, 2.0 parts of propoxylated butanol (30 P.O.) was added before homogenization and 0.3 parts of silicone oil was added after homogenization, as surface active agents.

#### EXAMPLE III.

(a) A composition was prepared according to Example I with the following exceptions. Five parts of silica was suspended in 71.7 parts of mineral oil, 1.0 part of amide was melted with 10.0 parts of mineral oil, and 2.0 parts of propoxylated butanol (30 P.O.) was added before homogenization.

(b) To Composition (a), above, was added 0.3 parts of silicone oil, as an additional surface-active agent, and 10.0 parts of an oil soluble polymer ("Paratone" 440).

#### EXAMPLE IV.

A composition was prepared according to Example III except that the oil soluble polymer was "Acryloid" 966.

#### EXAMPLE V.

A composition was prepared according to Example III except that the oil soluble polymer was "Lubrizol" 3702.

The compositions of this invention are useful in the manufacture of latex and other water-base paints. A defoamer is desirable in paints to prevent entrained air bubbles occurring as a result of handling, mixing, etc., from disfiguring the coated surface. The compositions of this invention can be added to the paint formulation at any time during its manufacture in proportions of 1 to 5 pounds per hundred gallons of formulated paint (1.2 grams/liter to 6.0 grams/liter) and preferably at about 3 pounds per hundred gallons (approximately 3.59 grams/liter).

The evaluation of these compositions as paint defoamers was as follows. A test for holddown of foam in a paint formulation was conducted by adding the composition to be tested to a latex paint containing no defoamer and shaking on a "Red Devil" Mixer (Regd. Trademark) for ten minutes. The shaken sample was then weighed and this weight was used to calculate the density of the paint (pounds/gallon) and the volume percentage of entrapped air. These figures were then compared with those for unshaken paint, and paint shaken without any defoamer.

Test results using the above method are as follows.

I. Shaker test using New London Mills' SBR paint, weighing 14.60 lbs/gal. shaken for 10 minutes with a 3.0 lb/100 gal. addition of defoamer.

Defoamer	Weight per gallons (lbs) after shaking	weight loss (lbs)	% of entrained air
1. Example III	14.52	0.08	0.55
2. "Foamkill" 639-C*	14.48	0.12	0.82
3. According to U.S. 3,207,698	14.40	0.20	1.37
4. Blank	12.12	2.48	17.00

\* a paint defoamer sold by Crucible Chemical Company, which is a liquid nonionic having a flash point of over 149°C.

II. Shaker test using Conchemco's Deep Base #6212 paint, weighing 10.45 lbs/gal. shaken for 5 minutes with a 6.0 lbs/100 gals. addition of defoamer.

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Defoamer	Weight per gallon (lbs)	weight loss (lbs)	% of entrained air
1. According to U.S. 3,207,698	10.08	0.37	3.54
2. Example III	9.72	0.73	6.98
3. Fales' No-Fo*	9.23	1.22	11.68
4. Blank	5.96	4.49	42.90

\* a commercially available paint defoamer.

III. A further test for film appearance was conducted using Conchemco's Deep Base #6212 (samples aged for one week at 49°C) with an addition of 6.0 lbs/100 gals.

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Defoamer	speed of bubble break	dried film appearance		
		bubbles	craters	pinholes
1. According to U.S. 3,207,698	fast	trace	trace	very few
2. Example III	moderate	few	moderate	moderate
3. Fales' No-Fo	very slow	many	many	many
4. Blank	very slow	extensive	extensive	extensive

15 The compositions of this invention are also  
20 useful in the manufacture of animal glue and  
25 other water-base adhesives. A defoamer is  
desirable in adhesives to prevent entrained  
air bubbles from reducing the surface contact  
area and thus the strength of the adhesive  
bond. The compositions of this invention can  
be added to adhesive formulations during  
the blending of ingredients in proportions of  
.05 to 0.5 (and preferably 0.1 to 0.3) parts  
by weight per 100 parts by weight of ad-  
hesive solids.

The evaluation of these compositions as  
adhesive defoamers was as follows. All parts  
are by weight unless otherwise indicated.

Forty parts of animal glue were combined  
with 60 parts of water at a temperature of

60—71° C. While agitating at a moderate  
speed, 3 or 4 drops of phenol were added to  
the mix. Thirty-five parts of corn syrup were  
added to 65 parts of the above mixture, while  
the above temperature and agitation were  
maintained. After thoroughly blending all  
components, the mixer was set at "high  
speed", at which point 0.5 parts of the de-  
foamer to be tested was introduced. High  
speed mixing was continued for five minutes  
(temp. 65.5° C), after which the sample was  
set aside to cool undisturbed. After reaching  
room temperature, the resultant gel surface  
was examined for bubbles and other surface  
irregularities.

Test results using various defoamers in the  
above procedure are as follows.

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Rank (descending desirability of appearance)	Defoamer Type	Surface Appearance of Glue	
		Fine Bubbles	Large Bubbles
1	Composition of this invention	few	none
2	quick-chilled amide base	few	very few
3	hydrophobic silica, aluminum stearate and polyoxyalkylene base	moderate	few
4	wax and PEG 400 stearate base	moderate	few
5	5:1 blend of nos. 2 and 3	moderate	few
6	hydrophobic silica and polyoxyalkylene base	many	moderate
7	polyoxyalkylene and aluminum stearate base	many	many
8	same as no. 3, but with different emulsifiers	many	many
9	blank	very many	very many

- 5 The compositions of this invention are also useful in paper manufacture for the reduction of existing foam (knock-down) and prevention of foam formation (hold-down) which occurs in black liquor during the pulping process. When used for this purpose, it is preferable to add 0.003 to 0.5 parts by weight of defoamer solids to the pulp, per 100 parts by weight of dry pulp. 30
- 10 The following apparatus and test method was used in determining the effectiveness of various compositions in knocking down and holding down foam in black liquor. The apparatus and method could, however, be used for testing any liquid which forms a foam upon agitation and/or heating. 35
- 15 A 1000 cc. tall form beaker is used as the primary container for the liquid to be tested. A curved glass outlet fused onto the base of the beaker is connected with a rubber hose to a centrifugal pump. The pump is used to circulate continuously the test liquid from the beaker into the pump and back into the beaker. Pumping is carried out at a rate so that the test liquid in the beaker is agitated by the re-entering test liquid to such an extent that foam forms. The pumping rate is about 40
- 20 two gallons per minute. Test liquid enters the beaker at a point about 6 centimeters above the surface of the liquid in the beaker and strikes the surface of the liquid in the beaker at an angle of 90°. 45
- 25 In carrying out the testing of the defoamer compositions, 500 cc. of freshly obtained concentrated black liquor is charged at about 75° C. into the beaker. This liquid, when quiescent, fills the beaker to a level of about 8.3 centimeters from the bottom. This level is marked and labeled the 0 line. In the test for hold down, 0.1 cc. of defoamer composition is added to the 500 cc. of test liquid in the beaker. The pump and stop watch are started simultaneously. Height of the foam above the 0 line is measured at 15 second intervals for the first minute, then at 30 second intervals, and recorded. In the test for knockdown, the liquor is agitated and heated prior to the addition of any defoamer composition. After a foam has built up to 8 centimeters, 0.1 cc. of the defoamer composition to be tested is added and the data are recorded as above. 50
- Test results using the above method are as follows. 55

## I. Hold-down Efficacy—Comparative Tests

Defoamer	Seconds: Foam height (mm)							
	15	30	45	60	90	120	150	180
1. Example I	24	17	16	20	28	37	47	58
2. Example II	9	1	4	10	17	25	34	44
3. Example III	12	10	13	17	26	32	38	48
4. Example IV	34	28	24	21	21	24	31	40
5. Commercial Silica Base	5	1	5	10	20	31	42	56
6. Commercial Quick-Chilled Amide Base	10	5	5	8	13	16	27	36

The above tests demonstrate that the compositions of this invention are effective defoamers compared to existing commercial defoamers of both the hydrophobic silica base and quick-chilled amide base types.

## II. Hold-down Efficacy—Comparative Tests with Increased Quick-Chilled Amide

Defoamer	Seconds: Foam height (mm)			
	15	30	45	60
1. 1% Quick-chilled stearic diamide of ethylene diamine+9% hydrophobic silica	14	18	23	29
2. 4% Quick-chilled stearic diamide of ethylene diamine+9% hydrophobic silica	14	19	28	36

The above test clearly demonstrates that increasing the amount of quick-chilled amide to the point where it may be expected to have defoaming efficacy is not useful. This indicates that the quick-chilled amide is clearly not utilized in this invention for its known property as a defoamer. In fact, it should be noted that not only does the combination of the known defoamers, hydrophobic silica and quick-chilled amide, not synergistically increase defoaming efficacy, it actually decreases it.

A test was designed to test the efficacy of the stabilized compositions falling within the scope of this invention as compared to compositions using other stabilizers and to non-stabilized hydrophobic silica defoamers.

A centrifuge containing the various compositions was run for 1 hour at 1,000 r.p.m. The test tubes of the centrifuge were each filled to a height of 106 mm with the compositions to be tested. The compositions of this invention, when they separated at all, usually did so into three phases: oil on top; oil and quick-chilled amide in the middle; and silica with some oil on the bottom. Compositions containing no quick-chilled amide separated into two phases: oil on top; and silica with some oil on the bottom. The first

number in the following table refers to the height of the non-silica layer or layers. The second number, refers to the viscosity of the composition before centrifuging.

All of the silicas used in the following test were hydrophobic and within the scope of this invention (unless otherwise noted). It will be seen that although fine and medium particle size silicas are preferred, large particle size silica can also be used, depending on the choice of quick-chilled amide. In this test, the large particle size silica used was actually an agglomerate of medium size particles.

The first two amides in the following test are quick-chilled and within the scope of this invention. The third amide is not quick-chilled.

Since a more viscous medium is generally considered to keep particles in suspension better than one which is less viscous, viscosity was measured for each composition (the figure in parenthesis). Compositions were prepared using polybutene as a thickening agent. Although these compositions were relatively stable, it should be noted that excessively large quantities of polybutene were required (25 and 21% respectively). A composition was also prepared using a fine particle size

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hydrophilic silica as a thickening agent. Although this composition was relatively stable, it should be noted that such silica is extremely expensive and of limited supply. In fact, one of the advantages of this invention is that fine particle silica is not required to achieve stability. The viscosity data (in parentheses) indicate that high viscosity alone is not sufficient to stabilize the silica suspension. This is apparent from comparing stabilizers nos. 2 and 6 combined with fine silica and

stabilizers nos. 2 and 4 combined with medium silica.

In interpreting the data, comparisons should be made vertically, that is, amongst various stabilizers using the same silica. The larger the silica, the more difficult the stabilization. Therefore, a height of 2 or less is acceptable for fine silica, a height of 5 or less is acceptable for medium silica, and a height of 10 or less is acceptable for large silica.

Combined Height of Phases One and Two (Viscosity)

Stabilizer (1%)	Silica (9%)—particle size—(oil absorption—gms/100 gms)		
	Fine (250)	Medium (170–190)	Large (125–165)
1. stearic diamide of ethylene diamine (quick-chilled)	0 (1600)	2 (1200)	10 (1300)
2. oleic diamide of ethylene triamine (quick-chilled)	1 (320)	4 (80)	70 (60)
3. same as no. 1 but not quick-chilled	—	13 (250)	—
4. polybutene (thickener)	0 (860)*	4 (460)**	—
5. 1.5% fine silica (hydrophilic)	—	2 (840)	—
6. none	3 (360)	20 (160)	70 (100)
* 25% polybutene			
** 21% polybutene			

## WHAT WE CLAIM IS:—

1. A defoamer composition, which comprises a suspension of 3% to 20% by weight of hydrophobic silica in a water-immiscible carrier liquid and, as a stabilizer for the suspension, 0.1% to 2.0% by weight of a quick-chilled amide.
2. A composition according to claim 1, in which the quick-chilled amide is the reaction product of ethylene-diamine and tallow fatty acid.
3. A composition according to claim 1 or 2, in which the hydrophobic silica has an oil absorption value of more than 170 grams per 100 grams of silica.
4. A composition according to any preceding claim, in which the carrier liquid is paraffinic mineral oil.
5. A composition according to any preceding claim, containing up to 3.0% by weight of a surface-active additive.
6. A composition according to any preceding claim, containing up to 25% by weight of an oil-soluble organic polymer.
7. A composition according to claim 6, in which the oil-soluble organic polymer is a copolymer of vinyl acetate and fumaric acid esterified with a tallow alcohol.
8. A composition according to claim 6, in which the oil-soluble organic polymer is a copolymer of styrene and a polyester.
9. A composition according to claim 6, in which the oil-soluble organic polymer is a copolymer of alkyl methacrylate and N-vinyl pyrrolidone.
10. A defoamer composition according to claim 1, substantially as herein described.
11. A process of manufacturing a hydrophobic silica base defoamer, which comprises forming a temporarily stable suspension of hydrophobic silica in a water immiscible carrier liquid heated to at least 100° C., cooling the suspension to room temperature or below, separately heating an amide optionally mixed with a water-immiscible carrier liquid until the amide is melted or is dissolved in the carrier liquid, maintaining the amide as a melt or solution at elevated temperature for at least 15 minutes, rapidly adding the amide to the suspension, so as to quick-chill the amide, and homogenizing the resultant hydrophobic silica/carrier liquid/quick-chilled amide mixture at a pressure of 1,000 to 5,000 p.s.i., the resulting suspension containing 3% to 20% by weight of the silica and

0.1% to 2.0% by weight of the amide.

12. A process according to claim 11, in which the quick-chilled amide is the reaction product of ethylene-diamine and tallow fatty acid.

13. A process according to claim 11 or 12, in which the hydrophobic silica has an oil absorption value of more than 170 grams per 100 grams of silica.

14. A process according to claim 11, 12 or 13, in which the carrier liquid is paraffinic mineral oil.

15. A process according to any of claims 11 to 14, in which a surface-active agent is added after homogenization.

16. A process according to any of claims 11 to 15, in which an oil-soluble organic polymer is added after homogenization.

17. A process according to claim 11, substantially as herein described.

18. A defoamer composition, when made by a process according to any of claims 11 to 17.

19. A method of defoaming black liquor present in paper manufacture, which comprises adding thereto a defoamer composition according to any of claims 1 to 10 or 18.

20. A method according to claim 19, in which the defoamer composition is added in an amount of 0.003 to 0.5 parts by weight of solids, per 100 parts by weight of dry paper pulp.

21. A method of foam prevention in water-base paints, which comprises incorporating therein a composition according to any of claims 1 to 10 or 18.

22. A method according to claim 21, in which the defoamer composition is incorporated in an amount of 1.2 to 6.0 grams of composition per litre of paint.

23. A method of foam prevention in water-base adhesives, which comprises incorporating therein a defoamer composition according to any of claims 1 to 10 or 18.

24. A method according to claim 23, in which the defoamer composition is incorporated in an amount of 0.05 to 0.5 parts by weight of composition per 100 parts by weight of adhesive solids.

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